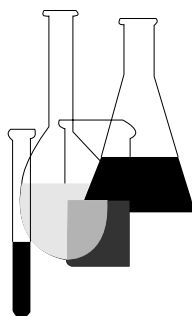




Fate, Transport and Transformation Test Guidelines

OPPTS 835.2310 Maximum Direct Photolysis Rate in Air from UV/Visible Spectroscopy



INTRODUCTION

This guideline is one of a series of test guidelines that have been developed by the Office of Prevention, Pesticides and Toxic Substances, United States Environmental Protection Agency for use in the testing of pesticides and toxic substances, and the development of test data that must be submitted to the Agency for review under Federal regulations.

The Office of Prevention, Pesticides and Toxic Substances (OPPTS) has developed this guideline through a process of harmonization that blended the testing guidance and requirements that existed in the Office of Pollution Prevention and Toxics (OPPT) and appeared in Title 40, Chapter I, Subchapter R of the Code of Federal Regulations (CFR), the Office of Pesticide Programs (OPP) which appeared in publications of the National Technical Information Service (NTIS) and the guidelines published by the Organization for Economic Cooperation and Development (OECD).

The purpose of harmonizing these guidelines into a single set of OPPTS guidelines is to minimize variations among the testing procedures that must be performed to meet the data requirements of the U. S. Environmental Protection Agency under the Toxic Substances Control Act (15 U.S.C. 2601) and the Federal Insecticide, Fungicide and Rodenticide Act (7 U.S.C. 136, *et seq.*).

Final Guideline Release: This guideline is available from the U.S. Government Printing Office, Washington, DC 20402 on *The Federal Bulletin Board*. By modem dial 202-512-1387, telnet and ftp: fedbbs.access.gpo.gov (IP 162.140.64.19), or call 202-512-0132 for disks or paper copies. This guideline is also available electronically in ASCII and PDF (portable document format) from EPA's World Wide Web site (<http://www.epa.gov/epahome/research.htm>) under the heading "Researchers and Scientists/Test Methods and Guidelines/OPPTS Harmonized Test Guidelines."

OPPTS 835.2310 Maximum direct photolysis rate in air from UV/visible spectroscopy.

(a) **Scope**—(1) **Applicability.** This guideline is intended to meet testing requirements of both the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (7 U.S.C. 136, *et seq.*) and the Toxic Substances Control Act (TSCA) (15 U.S.C. 2601).

(2) **Background.** The source material used in developing this harmonized OPPTS test guideline is 40 CFR 796.3800 Gas Phase Absorption Spectra and Photolysis.

(b) **Introduction**—(1) **Background and purpose.** Numerous chemicals enter the atmosphere from a variety of sources. For example, chemicals enter the atmosphere as a result of the burning of coal, from the combustion of gasoline in cars and diesel fuel in trucks, and from the release of volatile organic chemicals during manufacture, processing, use, and disposal. Pesticides, applied from airplanes, enter the atmosphere directly and volatilize from soils and water bodies. Chemical pollutants present in the atmosphere can undergo photochemical transformation in the environment by direct photolysis in sunlight. Quantitative data in the form of rate constants and half-lives are needed to determine the importance of direct photolysis of pollutants in the atmosphere. This test method describes a first-tier screening level test method to estimate the maximum direct photolysis rate constant and minimum half-life of chemicals in the atmosphere in sunlight as a function of latitude and season of the year in the United States.

(2) **Definitions and units.** The definitions in section 3 of TSCA and in 40 CFR Part 792—Good Laboratory Practice Standards (GLP) apply to this test guideline. The following definitions also apply to this test guideline.

Absorbance (A_λ) is defined as the logarithm of the ratio of the initial intensity (I_0) of a beam of radiant energy to the intensity (I) of the same beam after passage through a sample at a fixed wavelength λ . Thus, $A_\lambda = \log (I_0/I)$.

The *actinic solar irradiance in the atmosphere* (J_λ) is related to the sunlight intensity in the atmosphere and is proportional to the average light flux (in units of photons per square centimeter per day) that is available to cause photoreaction in the wavelength interval $\Delta\lambda$, centered at λ , over a 24-hour day at a specific latitude and season date. It is the irradiance which would be measured by a weakly absorbing spherical actinometer exposed to direct solar radiation and sky radiation from all directions.

The *Beer-Lambert law* states that the absorbance of a chemical in the gas phase, at a fixed wavelength, is proportional to the thickness of

the absorbing material (l), or the light pathlength, and the concentration of the absorbing species (C).

Cross section (σ_{λ}') is defined as the proportionality constant in the Beer-Lambert law. Thus, $A_{\lambda} = \sigma_{\lambda}' Cl$, where A_{λ} is the absorbance, C is the concentration in molecules per cubic centimeter and l is the pathlength in centimeters. The units of the cross section σ_{λ}' are square centimeters per molecule. Numerical values of the cross section depend upon the nature of the absorbing species.

Direct photolysis is defined as the direct absorption of light by a chemical followed by a reaction which transforms the parent chemical into one or more products.

A *first-order reaction* is defined as a reaction in which the rate of disappearance of a chemical is directly proportional to the concentration of the chemical and is not a function of the concentration of any other chemical present in the reaction mixture.

The Grotthus-Draper law, the first law of photochemistry, states that only light which is absorbed can be effective in producing a chemical transformation.

The *half-life* ($t_{1/2}$) of a chemical is defined as the time required for the concentration of the chemical being photolyzed to be reduced to one-half its initial value.

Radiant energy, or radiation, is defined as the energy traveling as a wave unaccompanied by transfer of matter. Examples include X-rays, visible light, UV light, radio waves, etc.

The *reaction quantum yield* (ϕ_{λ}) for an excited state process is defined as the fraction of absorbed light that results in photoreaction at a fixed wavelength λ . It is the ratio of a number of molecules that photoreact to the number of quanta of light absorbed or the ratio of the number of moles that photoreact to the number of einsteins of light absorbed at a fixed wavelength λ .

The *Stark-Einstein law*, the second law of photochemistry, states that only one molecule is activated to an excited state per photon or quantum of light absorbed.

The *sunlight direct photolysis rate constant* (k_{pE}) is the first-order rate constant (in units of day^{-1}) and is a measure of the rate of disappearance of a chemical in the gas phase in sunlight.

(3) Principle of the test method. (i) For weak absorbance of a chemical in the atmosphere, the first-order direct photolysis rate constant, k_{pe} , is given by the equation

Equation 1

$$k_{pE} = 2.30 \sum \phi_{\lambda} \sigma'_{\lambda} J_{\lambda}$$

where ϕ_{λ} is the reaction quantum yield; σ'_{λ} is the cross section (in units of $\text{cm}^2 \text{ molecule}^{-1}$) averaged over a wavelength interval $\Delta\lambda$, centered at λ ; J_{λ} is the actinic solar irradiance (in units of photons $\text{cm}^{-2} \text{ day}^{-1}$) averaged over the wavelength interval $\Delta\lambda$, centered at λ ; and the summation is taken over the range $\Delta\lambda = 290$ to 800 nm . J_{λ} is the solar actinic irradiance in the atmosphere under clear sky conditions and is a function of latitude and season of the year.

(ii) Since this photolysis process is first-order, the half-life ($t_{1/2}$) of a chemical is given by

Equation 2

$$t_{1/2} = 0.693/k_{pe}$$

(iii) A simple first-tier screening test has been developed using Equation 1. As an approximation, it is assumed that the reaction quantum yield ϕ_{λ} is equal to 1, the maximum value. As a result, the upper limit for the direct photolysis sunlight rate constant in the gas phase is obtained and Equation 1 becomes

Equation 3

$$(k_{pE})_{\max} = 2.30 \sum \sigma'_{\lambda} J_{\lambda}$$

Using Equation 3 in Equation 2, the lower limit for the half-life is given by

Equation 4

$$(t_{1/2})_{\min} = 0.693/(k_{pE})_{\max}$$

The cross section can be determined experimentally by the procedures outlined in paragraph (c) of this guideline and the values of J_{λ} are given in Tables 1 to 4 under paragraph (c)(3) of this guideline as a function of latitude and season of the year in the United States. These data can be used in Equation 3 to calculate $(k_{pE})_{\max}$. Finally, $(k_{pE})_{\max}$ can be substituted in Equation 4 to calculate $(t_{1/2})_{\min}$.

(4) **Applicability and specificity.** (i) This test method is applicable to all chemicals which have UV/visible absorptions in the range 290 to 800 nm. Some chemicals only have absorptions below 290 nm and consequently cannot undergo direct photolysis in sunlight (e.g. chemicals such as alkanes, alkenes, alkynes, dienes, and fluoroalkanes).

(ii) This test method is only applicable to pure chemicals and not to the technical grade.

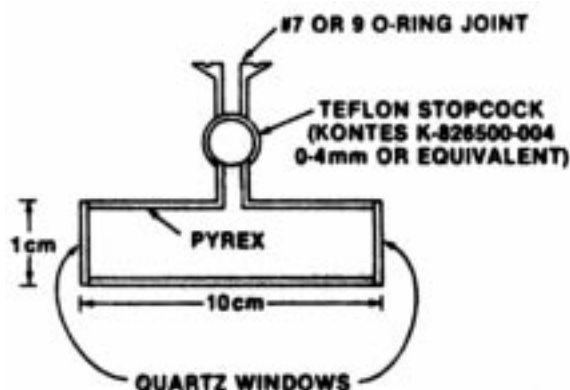
(iii) The first-tier screening test can be employed to estimate $(k_{pE})_{\max}$ and $(t_{1/2})_{\min}$. If these data indicate that gas phase photolysis is an important process relative to other gas phase transformation processes (e.g. oxidation with hydroxyl radicals or ozone), it is recommended that an upper-tier photolysis test be carried out to determine the reaction quantum yield and thus obtain more precise environmentally relevant rate constants and half-lives in sunlight. The data obtained from this first-tier test method can be used to determine $(k_{pE})_{\max}$ for a test chemical as a function of latitude and season of the year in the United States under clear sky conditions. These rate constants are in a form suitable for preliminary mathematical modeling for environmental fate of a test chemical.

(c) **Test procedures.** The procedures outlined in this test method are based on the method proposed by Mill et al. under paragraph (e)(1) of this guideline and developed by Pitts et al. under paragraph (e)(2) of this guideline. It is also recommended that OPPTS 830.7050 be consulted for additional guidance.

(1) **Test conditions**—(i) **UV/visible spectrophotometer.** Although single-beam spectrophotometers may be used, recording double beam spectrophotometers are recommended. It is extremely important that the spectrophotometer be able to scan over the wavelength region 270 to 800 nm and have an absorbance sensitivity, at a signal/noise ratio of one, of approximately 0.001. It is important that the spectrophotometer be able to attain a 90 percent separation of two monochromatic spectral features approximately 4 nm apart, peak to peak (i.e. the resolution should be at least 4 nm). It is also desirable to have a spectrophotometer that can accommodate absorption cells of length ≥ 10 cm. A Cary 219 UV/Visible Spectrophotometer, or an equivalent model, is recommended.

(ii) **Vapor and liquid absorption cells.** (A) Long pathlength cells are preferable; however, many commercial spectrophotometers will only accept absorption cells of 10 cm or less. A suitable vapor cell is depicted in the following Figure 1.

FIGURE 1—GAS ABSORPTION CELL

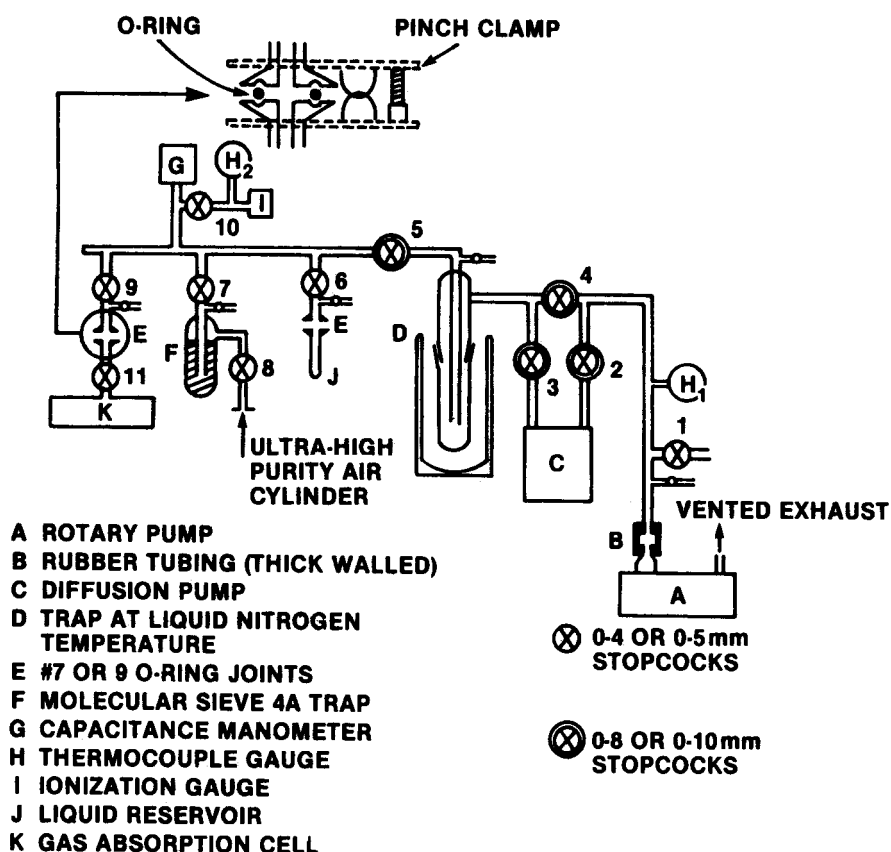


(B) A suitable vapor cell can be constructed as follows. The vapor cell should be constructed of Pyrex, 1 cm O.D. and 10 cm in length, and be fitted with plane parallel quartz windows at each end. The quartz windows can be conveniently attached to the Pyrex cell with vacuum tight epoxy resin (e.g. Torr-Seal, Varian Associates) only applied to the outside surface. A Teflon stopcock (or a Pyrex O-ring stopcock) should be connected to the cell and contain an O-ring joint. The O-ring joint (e.g. no. 7 or no. 9, Kontes or Ace Glass) must match the one on the vacuum rack. Viton O-rings are recommended and should be frequently inspected for signs of deterioration which would result in vacuum leaks. A matched reference cell is extremely useful but not essential. However, the sample and reference cells should be very similar. Small spectral differences between the cells can be compensated for by running a blank with the sample and reference cells in the spectrophotometer. The use of stopcock grease is not required with these cells and should be avoided.

(C) A matched pair of liquid absorption cells is very desirable but is not essential. A pair of quartz UV absorption cells, 10 cm in length, having ground glass or Teflon stoppers are recommended. These liquid absorption cells are readily available commercially.

(iii) **Vacuum gas handling system.** A suitable gas handling system is shown diagrammatically in the following Figure 2 and should be constructed completely with Pyrex glass.

FIGURE 2—SCHEMATIC OF GAS HANDLING VACUUM RACK



The components of the gas handling system are discussed below. The use of stopcock grease is not required and should be avoided.

(A) **Vacuum pumping system.** (1) In order to achieve a good vacuum, i.e. pressures $<10^{-5}$ torr (1.3×10^{-6} kPa), two pumps are required. The forepump (A) must be capable of achieving a pressure <0.05 torr (0.0065 kPa). A rotary pump (e.g. a Welch Model 1402 Duo-Seal or an equivalent model) is recommended. The forepump can be attached to the vacuum system by means of heavy-walled rubber vacuum tubing (B), or any flexible vacuum tubing. The exhaust from this pump should be vented into a hood.

(2) The second pump, a high vacuum model, should be a multistage oil diffusion pump (C) (e.g. a Consolidated Vacuum Corp. VMF-10 or VMF-20 or an equivalent model). The pump fluid should be a silicone oil with a room temperature vapor pressure of $\leq 10^{-6}$ torr (1.3×10^{-7} kPa) (e.g. Dow-Corning D.C. 702 or 703, or an equivalent grade).

(3) It is extremely important that the pumping system contain a trap (D) cooled with liquid nitrogen. The cone and socket joint on this trap can be conveniently sealed with Apiezon W wax, or an equivalent grade. This wax requires only gentle heating to apply and makes an effective vacuum seal. It is possible that a few test chemicals could dissolve Apiezon W wax. In this case, an inert silicone grease may be used to seal the trap.

(B) **Vacuum rack.** The recommended vacuum rack assembly is depicted in Figure 2 under paragraph (d)(1)(iii) of this guideline. All stopcocks should be of Teflon with Viton O-rings (Kontes K-826500 or K-826510 series or equivalent grades (or Pyrex O-ring stopcocks)). The O-ring joints (E) (no. 7 or no. 9) must be compatible with those on the gas absorption cell (K) or on the liquid reservoir (J). These O-ring joints should be clamped by pinch clamps with a screw lock device (e.g. Thomas #18A, or an equivalent grade).

(C) **Pressure Gauges.** Three pressure gauges are required:

(1) An ionization gauge to measure high vacuum ($<10^{-3}$ torr (1.3×10^{-4} kPa)).

(2) A thermocouple gauge to monitor the pressure in the range 10^{-3} to 1 torr (1.3×10^{-4} to 0.13 kPa). A convenient pressure monitoring system which contains ionization and thermocouple gauges is a Consolidated Vacuum Corp. Model GIC-300A or an equivalent model.

(3) A pressure gauge to monitor the pressure of the test chemical and diluent in the range 0.01 to 760 torr (0.0013 to 101.3 kPa); for example, an MKS Baratron 310 BHS-1000 with the associated 170-6C electronics unit and a digital readout or an equivalent model. While this vacuum gauge exhibits a slow zero drift, it can be readily rezeroed using the ionization gauge, i.e. when the ionization gauge reads approximately 10^{-3} torr (0.00013 kPa) or less.

(2) **Operation of the gas handling system.** Since there are a wide variety of procedures available for operating a gas handling system, the method used is left to the discretion of the tester. For those testers who do not have experience in handling a vacuum system, the detailed procedure described in paragraph (d)(5) of this guideline is recommended.

(3) **Preparation of samples—(i) Preparation of the gas phase test chemical sample: Preliminary Steps.** (A) If the test chemical is a gas at room temperature, attach the gas container to the O-ring at the point where the liquid reservoir (J) is placed. Close stopcocks 2 and 3 and open 4. Pump until the pressure is $<10^{-2}$ torr (1.3×10^{-3} kPa) as read on thermocouple gauge (H2). Then open stopcocks 2 and 3 and close 4 and pump until the pressure is less than 10^{-5} torr (1.3×10^{-6} kPa) as read on the ionization gauge (I).

(B) If the test chemical is a liquid at room temperature, add a few cubic centimeters of liquid to a reservoir tube (J), sealed at one end and containing an O-ring at the other end, and connect the tube via the O-ring to stopcock 6. Freeze the sample with a Dewar containing liquid nitrogen, close stopcocks 2 and 3 and open 4 and 6. Degas the test chemical by allowing it to warm up to the liquid state, briefly degas, and refreeze the liquid. Repeat this process three or more times until the evolution of gas bubbles ceases upon thawing. Freeze the liquid, open stopcocks 2 and 3 and close 4. Pump until the pressure is less than 10^{-5} torr (1.3×10^{-6} kPa) as indicated by the ionization gauge (I). Close stopcock 6.

(ii) Introduction of the test chemical into the gas absorption cell.

(A) For introduction of the test chemical into the gas absorption cell, close stopcocks 5, 7 and 10, with 9 and 11 open. If the test chemical is a gas, stopcock 6 should be opened and the gas container valve is gradually opened to admit the gas into the gas handling manifold and gas absorption cell until the desired pressure is attained, as read on the capacitance manometer (G). Close the gas container valve and stopcock 6 and allow approximately 5 min before the final pressure at (G) is read. If the pressure has not stabilized in approximately 5 min allow the cell to condition for several hours before the final pressure at (G) is read.

(B) For a liquid chemical in the reservoir (J), which has been degassed and is at liquid nitrogen temperature, the liquid nitrogen Dewar should be removed and stopcock 6 opened. The cold liquid in the reservoir (J) is allowed to warm up until the required pressure is attained, as read by the capacitance manometer (G). Close stopcock 6 and cool the reservoir again with liquid nitrogen and allow approximately 5 min before the final pressure at (G) is read. If the pressure has not stabilized in approximately 5 min, allow the cell to condition for several hours before the final pressure at (G) is read.

(C) With stopcocks 6, 8 and 11 closed and 5, 7, 9, and 10 open, the gas handling manifold is evacuated as described previously to a pressure less than 10^{-5} torr (1.3×10^{-6} kPa). Stopcocks 5 and 10 are then closed and ultra-high purity air from a cylinder is admitted into the gas handling manifold via stopcock 8 and through the trap (F) containing Molecular Sieve 4A. When the manifold is at one atmosphere pressure, as measured by pressure gauge (G), stopcock 11 is briefly opened to pressure the gas absorption cell to one atmosphere, and then closed. Stopcocks 8 and 9 are closed and the gas handling system is evacuated as described previously. The gas absorption cell can then be removed from (E) and covered to avoid photolysis.

(D) Based on the pressure P of the test chemical, as measured by gauge (G), the concentration of the gas sample is

Equation 5

$$C \text{ (molecules cm}^{-3}\text{)} = 9.657 \times 10^{18} P(\text{torr})/T(\text{ K})$$

Equation 5a

$$C \text{ (molecules cm}^{-3}\text{)} = 1.287 \times 10^{18} P(\text{kPa})/T(\text{K})$$

where T is the room temperature in degrees Kelvin, which should be routinely monitored with a thermometer.

(F) The recommended pressure of the test chemical should be in the range 1–5 torr (0.13–0.65 kPa) where the Beer-Lambert law is obeyed. A final check on whether the test chemical obeys the Beer-Lambert law can be accomplished by demonstrating the constancy of the cross section at three partial pressures differing by a factor of 10.

(iii) **Preparation of solution phase test chemical sample.** (A) If the properties of the test chemical (i.e. small cross sections, low vapor pressure) are such that the maximum absorbance obtainable is one-tenth of the most sensitive spectrophotometer scale or less (i.e. ≤ 0.001 absorbance), a solution-phase study should be undertaken. The most sensitive scale may be limited by inherent spectrophotometer noise. For example, a given spectrophotometer's most sensitive scale is 0.00 to 0.10 absorbance units. Therefore, a test chemical for which the product of its maximum cross section and its concentration is less than 0.001 (in a 10 cm cell) could not be analyzed in the vapor phase with this particular spectrophotometer.

(B) The following spectroscopic grade chemicals are recommended to prepare solutions: chloroform, *n*-hexane, acetonitrile, and cyclohexane. Solutions of up to 10 percent by volume of test chemical can be prepared in one of these solvents in the standard manner.

(C) The concentration of the test chemical is given by the following equations

Equation 6

$$C \text{ (molecules cm}^{-3}\text{)} = 6.022 \times 10^{23} \text{ mass (gms)}/\text{FW (V}_d\text{)}$$

Equation 6a

$$C \text{ (molecules cm}^{-3}\text{)} = 6.022 \times 10^{23} V_s \rho / \text{FW (V}_d\text{)}$$

where V_s is the volume of test chemical delivered into a volume V_d of solvent cubic centimeters, FW is the formula weight of the test chemical in grams, and ρ is the density of the test chemical in grams per cubic centimeter at the room temperature the solution was prepared.

(4) **Procedure for obtaining the spectrum.** As a general guide to obtaining UV/visible absorption spectra, the procedures outlined in OPPTS 830.7050 are recommended. Since the method presented in this procedure

was developed by Pitts et al. (1981), it is recommended that this report be consulted for further details.

(i) **Determination of the cell pathlength.** The method for determining the cell pathlength of gas or liquid cells is left to the discretion of the tester. However, the method listed in OPPTS 830.7050, using one of the reference compounds, is recommended.

(ii) **Gas phase spectrum.** Measure the absorbance of the test chemical in duplicate relative to a matched cell filled with ultra-high purity air from the same cylinder similarly passed through trap (F) containing the molecular sieve. The absorbance should be measured at wavelengths $\lambda \geq 280$ nm using minimum slit widths. Record, in duplicate, the baseline when both the same reference cells are filled with high purity air dried through the molecular sieve and at the same settings as used for the test chemical sample. These data will be used to calculate the cross section, σ'_λ , at the appropriate wavelength intervals, centered at wavelength λ , listed in Tables 1 through 4, under paragraph (d)(3) of this guideline.

(iii) **Solution phase spectrum.** (A) Measure the absorbance of the test chemical in duplicate relative to a matched cell containing the solvent. The absorbance should be measured for wavelengths $\lambda \geq 280$ nm using the minimum slit widths. Record, in duplicate, the baseline when both the sample and reference cells are filled with the solvents. These data will be used to calculate the cross sections, σ'_λ , for the appropriate wavelength intervals, centered at λ , listed in Tables 1 through 4 under paragraph (d)(3) of this guideline.

(B) The concentration of the test chemical should be in the range where the Beer-Lambert law is obeyed. A check on whether the test chemical obeys this law can be accomplished by demonstrating the constancy of the cross section at three concentrations differing by a factor of 10.

(d) **Data and reporting—(1) Treatment of results—(i) Determination of the cross section from the gas phase spectrum.** (A) The cross section, σ_λ , can be determined from the gas phase absorption spectrum and the Beer-Lambert law in the form

Equation 7

$$\sigma'_\lambda = A_\lambda / Cl$$

where A_λ is the absorbance at wavelength λ , centered in the wavelength interval $>\lambda$, C is the concentration of test chemical in molecules per cubic centimeter, and l is the cell pathlength in centimeters. The cross section of the test chemical should be determined for the wavelength intervals listed in Tables 1 through 4 under paragraph (d)(3) of this guideline.

(B) There are at least three nondestructive methods of determining the absorbance over a specified wavelength interval: estimation, square counting, and planimetry. For many spectra, estimating an average absorbance over a small wavelength interval is sufficient to yield accurate results. However, for spectra containing rapidly changing absorptions and complex fine structure, square counting or planimetry should be used. These two methods require the integration of a definite region (in $A_\lambda \times \text{nm}$) followed by division by the width of the region in nm to obtain absorbance. The method using a compensating polar planimeter is the most accurate and is recommended. The absorbance should be obtained from the average of three tracings.

(ii) **Determination of the cross section from the solution phase spectrum.** The cross section, σ'_λ , can be determined from the solution phase spectrum using Equation 7 for the wavelength intervals listed in Tables 1 through 4 under paragraph (d)(3) of this guideline. For solution spectra, estimating an average absorbance over the wavelength intervals is sufficient to yield accurate results.

(iii) **Estimation of the maximum direct photolysis rate constant and minimum half-life in the gas phase.** (A) Using the cross sections obtained from the spectra and the values of J_λ from Tables 1–4 under paragraph (d)(3) of this guideline, the maximum direct photolysis rate constant $(k_{\text{pE}})_{\text{max}}$ can be calculated at a specific latitude and season for the year using Equation 3. The minimum half-life, $(t_{1/2\text{E}})_{\text{min}}$, can be calculated using this $(k_{\text{pE}})_{\text{max}}$ in Equation 4.

(B) An example is presented in under paragraph (d)(4) of this guideline, to illustrate how the test data obtained in this section can be used.

(2) **Test data report.** (i) Submit the original chart, or photocopy, containing a plot of absorbance vs. wavelength plus the baseline. Spectra should include a readable wavelength scale, preferably marked at 10 nm intervals. Each spectrum should be clearly marked.

(ii) Gas phase spectra. (A) Report the pressure of the test chemical in torr (or kPa), the concentration in molecules per cubic centimeter, and the pathlength of the sample cell in centimeters. Describe the method used to determine the pathlength and report the experimental data.

(B) Report the wavelength λ , the wavelength interval for each 10 nm over the region of absorption, the value of the absorbance (A_λ) for each replicate, the mean absorbance, and the mean cross section in square centimeters per molecule.

(C) Report the estimated maximum direct photolysis rate constant in units of reciprocal days and the corresponding minimum half-life in days at 20°, 30°, 40°, and 50° north latitude for the summer and winter solstices.

(iii) Solution phase spectra. (A) Report the concentration of the test chemical in molecules per cubic centimeter, the type of cell used (quartz or borosilicate), and the pathlength in centimeters, the method used to determine the pathlength and report the experimental results.

(B) Report the identity of the solvent.

(C) Report the wavelength λ , the wavelength interval over the region of absorption, the value of the absorbance (A_λ) of each replicate, the mean absorbance, and the mean cross section square centimeter per molecule.

(D) Report the estimated maximum direct photolysis rate constant in days⁻¹ and the corresponding minimum half-life in days at 20°, 30°, 40°, and 50° north latitude for the summer and winter solstices.

(iv) Report the name, structure, and purity of the test chemical.

(v) Submit a recent spectrum on appropriate reference chemicals for photometric and wavelength accuracy.

(vi) Report the name and model of the spectrophotometer used.

(vii) Report the various control settings employed with the spectrophotometer. These might include scan speed, slit width, given, etc.

(viii) Report anything unusual about the test; e.g. if the Beer-Lambert law is not obeyed at a pressure of 1 to 5 torr (0.13 to 0.65 kPa), report the pressure at which the deviation was overcome and the experimental data. If the Beer-Lambert law is not obeyed in solution at high concentrations, report the concentration at which the deviation was overcome and the experimental data.

(ix) Report any other relevant information.

(3) Tables of solar irradiance

Table 1— J_λ Values at 20°N. Latitude

Wavelength center ^b	Summer solstice ^a	Equinox ^a	Winter solstice ^a	Wave-length center ^b	Fall or winter average ^a	Spring or summer average ^a	Wavelength center ^b
290	0.0000811	0.00000131	0.000000108	290	0.000000896	0.0000625	290
300	0.0810	0.0611	0.0212	300	0.0359	0.0769	300
310	1.10	0.9148	0.499	310	0.663	1.05	310
320	2.74	2.35	1.52	320	1.855	2.62	320
330	4.82	4.20	2.90	330	3.42	4.63	330
340	5.27	4.61	3.28	340	3.82	5.06	340
350	5.94	5.22	3.77	350	4.36	5.71	350
360	6.22	5.47	4.01	360	4.61	5.98	360
370	7.76	6.84	5.06	370	5.79	7.46	370
380	7.60	6.71	5.02	380	5.71	7.31	380
390	7.77	6.88	5.19	390	5.88	7.48	390
400	10.6	9.44	7.17	400	8.10	10.2	400
410	13.5	12.0	9.17	410	10.3	13.0	410
420	14.1	12.5	9.65	420	10.8	13.6	420
430	14.3	12.7	9.85	430	11.1	13.7	430
440	15.8	14.1	11.0	440	12.2	15.2	440
450	18.2	16.2	12.7	450	14.1	17.5	450
460	19.7	17.5	13.7	460	15.3	18.9	460
470	20.2	18.1	14.2	470	15.8	19.5	470

Table 1— J_{λ} Values at 20° N. Latitude—Continued

Wavelength center ^b	Summer solstice ^a	Equinox ^a	Winter solstice ^a	Wave-length center ^b	Fall or winter average ^a	Spring or summer average ^a	Wavelength center ^b
480	20.5	18.3	14.4	480	16.0	19.8	480
490	20.6	18.4	14.5	490	16.1	19.8	490
500	20.9	18.7	14.8	500	16.4	20.2	500
510	21.1	18.8	14.9	510	16.4	20.3	510
520	21.1	18.9	14.9	520	16.5	20.3	520
530	21.3	19.0	15.1	530	16.7	20.5	530
540	21.2	19.0	15.0	540	16.6	20.4	540
550	21.1	18.8	14.9	550	16.5	20.3	550
560	21.3	19.0	15.1	560	16.7	20.5	560
570	21.6	19.3	15.3	570	16.9	20.8	570
580	22.1	19.7	15.7	580	17.3	21.2	580
590	22.3	19.9	15.8	590	17.5	21.5	590
600	22.5	20.0	15.9	600	17.6	21.6	600
610	22.6	20.2	16.0	610	17.7	21.8	610
620	22.6	20.1	16.1	620	17.7	21.8	620
630	22.6	20.1	16.2	630	17.7	21.7	630
640	23.1	20.6	16.6	640	18.2	22.3	640
650	23.6	21.1	16.9	650	18.6	22.8	650
660	24.0	21.4	17.2	660	18.9	23.1	660
670	24.3	21.7	17.4	670	19.2	23.4	670
680	24.3	21.7	17.5	680	19.2	23.4	680
690	24.3	21.7	17.5	690	19.2	23.4	690
700	24.2	21.7	17.5	700	19.2	23.0	700
710	24.1	21.5	17.4	710	19.1	23.2	710
720	23.9	21.4	17.3	720	19.0	23.0	720
730	23.8	21.3	17.2	730	18.9	22.9	730
740	23.6	21.1	17.2	740	18.8	22.8	740
750	23.5	21.0	17.1	750	18.7	22.6	750
760	23.3	20.9	17.0	760	18.6	22.5	760
770	23.2	20.8	16.9	770	18.5	22.3	770
780	23.1	20.6	16.8	780	18.4	22.2	780
790	22.9	20.5	16.7	790	18.3	22.1	790
800	22.8	20.4	16.7	800	18.2	21.9	800

^a J_{λ} values are in units of 10^{19} photons $\text{cm}^{-2} \text{day}^{-1}$.

^b Wavelength intervals are uniformly 10 nm wide, extending from 5 nm lower than the center wavelength to 5 nm higher. Thus, the first interval centered on 290 extends from 285–295 nm

Table 2— J_{λ} Values at 30° N. Latitude

Wavelength center ^b	Summer solstice ^a	Equinox ^a	Winter solstice ^a	Wave-length center ^b	Fall or winter avg. ^a	Spring or summer avg. ^a	Wavelength center ^b
290	0.0000768	0.00000203	0.000000213	290	0.000000457	0.0000352	290
300	0.0831	0.0457	0.00835	300	0.0208	0.0704	300
310	1.14	0.787	0.300	310	0.480	1.02	310
320	2.84	2.13	1.06	320	1.47	2.60	320
330	5.02	3.88	2.13	330	2.81	4.62	330
340	5.49	4.30	2.48	340	3.19	5.08	
350	6.28	4.88	2.89	350	3.68	5.74	350
360	6.49	5.15	3.10	360	3.91	6.02	360
370	8.09	6.45	3.95	370	4.94	7.51	370
380	7.93	6.25	3.95	380	4.91	7.37	380
390	8.12	6.53	4.12	390	5.08	7.55	390
400	11.1	8.97	5.73	400	7.02	10.4	400
410	14.1	11.4	7.37	410	8.99	13.2	410
420	14.7	12. .	7.81	420	9.46	13.7	420
430	14.9	12.2	8.00	430	9.66	13.9	430
440	16.5	13.5	8.94	440	10.8	15.4	440
450	19.0	15.5	10.4	450	12.4	17.8	450
460	20.6	16.8	11.3	460	13.5	19.2	460
470	21.2	17.3	11.7	470	13.9	19.8	470
480	21.5	17.6	11.9	480	14.2	20.1	480
490	21.5	17.7	12.0	490	14.3	20.1	490
500	21.9	18.0	12.2	500	14.5	20.5	500
510	22.1	18.1	12.3	510	14.6	20.6	510
520	22.1	18.1	12.4	520	14.7	20.7	520
530	22.3	18.3	12.5	530	14.8	20.9	530
540	22.1	18.2	12.4	540	14.7	20.6	540
550	22.1	18.1	12.4	550	14.7	20.6	550
560	22.6	18.3	12.5	560	14.8	20.8	560
570	22.6	18.6	12.7	570	15.1	21.1	570
580	23.1	19.0	13.0	580	15.4	21.6	580
590	23.3	19.2	13.2	590	15.6	21.8	590

Table 2— J_{λ} Values at 30° N. Latitude—Continued

Wavelength center ^b	Summer solstice ^a	Equinox ^a	Winter solstice ^a	Wave-length center ^b	Fall or winter avg. ^a	Spring or summer avg. ^a	Wavelength center ^b
600	23.5	19.3	13.3	600	15.7	22.0	600
610	23.7	19.5	13.4	610	15.8	22.1	610
620	23.6	19.3	13.6	620	15.9	22.1	620
630	23.6	19.2	13.7	630	16.0	22.1	630
640	24.2	19.8	14.0	640	16.3	22.6	640
650	24.7	20.4	14.2	650	16.7	23.1	650
660	25.1	20.7	14.4	660	16.9	23.5	660
670	25.4	21.0	14.7	670	17.2	23.8	670
680	25.4	21.0	14.7	680	17.2	23.8	680
690	25.4	21.0	14.8	690	17.3	23.8	690
700	25.3	21.0	14.8	700	17.3	23.7	700
710	25.2	20.8	14.7	710	17.2	23.6	710
720	25.0	20.7	14.6	720	17.1	23.4	720
730	24.9	20.6	14.6	730	17.0	23.3	730
740	24.7	20.5	14.5	740	16.9	23.2	740
750	24.6	20.4	14.5	750	16.8	23.0	750
760	24.4	20.3	14.4	760	16.8	22.9	760
770	24.3	20.1	14.3	770	16.7	22.7	770
780	24.1	20.0	14.3	780	16.6	22.6	780
790	24.0	19.9	14.2	790	16.5	22.5	790
800	23.8	19.8	14.2	800	16.4	22.3	800

^a J_{λ} values are in units of 10^{19} photons cm^{-2} day⁻¹.

^bWavelength intervals are uniformly 10 nm wide, extending from 5 nm lower than the center wavelength to 5 nm higher. Thus, the first interval centered on 290 extends from 285–295 nm

Table 3— J_{λ} Values at 40° N. Latitude

Wavelength center ^b	Summer solstice ^a	Equinox ^a	Winter solstice ^a	Wave-length center ^b	Fall or winter avg. ^a	Spring or summer avg. ^a	Wavelength center ^b
290	1.36×10^{-5}	1.21×10^{-7}	6.15×10^{-10}	290	8.14×10^{-8}	3.49×10^{-6}	290
300	0.0769	0.0293	0.00145	300	0.00939	0.0587	300
310	1.12	0.618	0.132	310	0.298	0.940	310
320	2.87	1.81	0.591	320	1.04	2.49	320
330	5.11	3.41	1.31	330	2.90	4.49	330
340	5.62	3.83	1.58	340	2.43	4.77	340
350	6.35	4.39	1.88	350	2.84	5.64	350
360	6.61	4.65	2.05	360	3.05	5.93	360
370	8.32	5.86	2.64	370	3.88	7.43	370
380	8.17	5.80	2.67	380	3.88	7.30	380
390	8.37	5.99	2.82	390	4.05	7.50	390
400	11.5	8.26	3.97	400	5.64	10.3	400
410	14.6	10.5	5.15	410	7.26	13.1	410
420	15.2	11.1	5.51	420	7.69	13.9	420
430	15.5	11.3	6.69	430	7.89	15.4	430
440	17.1	12.5	6.41	440	8.82	17.8	440
450	19.7	14.5	7.47	450	10.2	19.2	450
460	21.3	15.7	8.15	460	11.1	19.8	460
470	22.0	16.2	8.51	470	11.5	20.1	470
480	22.3	16.5	8.74	480	11.8	20.2	480
490	22.3	16.6	8.83	490	11.9	20.6	490
500	22.7	16.9	8.99	500	12.1	20.7	500
510	22.9	17.0	9.07	510	12.2	20.8	510
520	22.9	17.0	9.14	520	12.3	21.0	520
530	23.2	17.2	9.24	530	12.4	21.0	530
540	23.0	17.1	9.18	540	12.3	20.8	540
550	22.9	17.0	9.15	550	12.3	20.7	550
560	23.1	17.2	9.23	560	12.4	20.9	560
570	23.5	17.4	9.38	570	12.6	21.2	570
580	24.0	17.8	9.62	580	12.9	21.9	580
590	24.2	18.0	9.79	590	13.1	21.9	590
600	24.4	18.2	9.85	600	13.2	22.1	600
610	24.6	18.3	9.93	610	13.2	22.2	610
620	24.5	18.3	10.2	620	13.4	22.2	620
630	24.5	18.3	10.2	630	13.5	22.1	630
640	25.1	18.8	10.5	640	13.8	22.7	640
650	25.7	19.2	10.7	650	14.1	23.3	650
660	26.1	19.5	10.9	660	14.3	23.6	660
670	26.4	19.8	11.1	670	14.5	24.0	670
680	26.3	19.9	11.1	680	14.6	24.0	680
690	26.4	19.9	11.2	690	14.6	24.0	690
700	26.4	19.9	11.3	700	14.7	24.0	700
710	26.2	19.8	11.2	710	14.6	23.9	710

Table 3— J_{λ} Values at 40° N. Latitude—Continued

Wavelength center ^b	Summer solstice ^a	Equinox ^a	Winter solstice ^a	Wave-length center ^b	Fall or winter avg. ^a	Spring or summer avg. ^a	Wavelength center ^b
720	26.1	19.7	11.2	720	14.6	23.7	720
730	25.9	19.6	11.2	730	14.5	23.5	730
740	25.8	19.5	11.2	740	14.5	23.4	740
750	25.6	19.4	11.2	750	14.4	23.3	750
760	25.5	19.3	11.2	760	14.4	23.1	760
770	25.3	19.2	11.3	770	14.3	23.0	770
780	25.2	19.1	11.3	780	14.3	22.4	780
790	25.0	19.0	11.2	790	14.2	22.7	790
800	24.8	1.89	11.2	800	14.1	22.6	800

^a J_{λ} values are in units of 10^{19} photons cm^{-2} day⁻¹.

^b Wavelength intervals are uniformly 10nm wide, extending from 5 nm lower than the center wavelength to 5 nm higher. Thus, the first interval centered on 290 extends from 285–295 nm

Table 4— J_{λ} Values at 50° N. Latitude

Wavelength center ^b	Summer solstice ^a	Equinox ^a	Winter solstice ^a	Wave-length center ^b	Fall or winter avg. ^a	Spring or summer avg. ^a	Wavelength center ^b
290	0.00000185	0.000000200	0.000000112	290	0.0000000391	0.00000152	290
300	0.0635	0.0140	0.0000681	300	0.00296	0.0433	300
310	1.05	0.423	0.321	310	0.147	0.810	310
320	2.81	1.41	0.214	320	0.610	2.28	320
330	5.10	2.78	0.555	330	1.33	4.23	330
340	5.64	3.19	0.711	340	1.59	4.73	340
350	6.41	3.70	0.864	350	1.88	5.40	350
360	6.70	3.96	0.953	360	2.04	5.71	360
370	8.46	5.03	1.25	370	2.63	7.18	370
380	8.32	5.01	1.28	380	2.66	7.09	380
390	8.56	5.21	1.37	390	2.80	7.31	390
400	11.8	7.22	1.95	400	3.93	10.1	400
410	15.0	9.27	2.57	410	5.09	12.8	410
420	15.7	9.79	2.79	420	5.45	13.5	420
430	15.9	10.0	2.92	430	5.62	13.7	430
440	17.6	11.2	3.33	440	6.33	15.2	440
450	20.3	12.9	3.92	450	7.37	17.6	450
460	22.0	14.0	4.31	460	8.05	19.0	460
470	22.7	14.5	4.54	470	8.40	19.7	470
480	23.1	14.8	4.70	480	8.62	20.0	480
490	23.1	15.0	4.78	490	8.72	20.1	490
500	23.5	15.2	4.88	500	8.87	20.4	500
510	23.7	15.3	4.94	510	9.00	20.6	510
520	23.8	15.4	4.98	520	9.03	20.6	520
530	24.0	15.6	5.05	530	9.12	20.8	530
540	23.8	15.5	5.02	540	9.07	20.7	540
550	23.7	15.4	5.01	550	9.05	20.6	550
560	24.0	15.5	5.04	560	9.11	20.8	560
570	24.3	15.8	5.11	570	9.26	21.1	570
580	24.8	16.1	5.27	580	9.50	21.6	580
590	25.1	16.4	5.38	590	9.66	21.8	590
600	25.3	16.5	5.42	600	9.73	22.0	600
610	25.5	16.6	5.47	610	9.80	22.1	610
620	25.4	16.8	5.61	620	9.96	22.1	620
630	25.3	17.0	5.77	630	10.1	22.1	630
640	26.0	17.3	5.93	640	10.4	22.7	640
650	26.7	17.6	6.10	650	10.6	23.3	650
660	27.1	17.8	6.24	660	10.8	23.6	660
670	27.5	18.1	6.39	670	11.0	24.0	670
680	27.5	18.2	6.47	680	11.0	24.0	680
690	27.5	18.2	6.56	690	11.1	24.0	690
700	27.5	18.2	6.64	700	11.2	24.0	700
710	27.3	18.1	6.67	710	11.2	29.9	710
720	27.2	18.1	6.72	720	11.2	23.8	720
730	27.0	18.0	6.75	730	11.2	23.6	730
740	26.9	17.9	6.78	740	11.2	23.5	740
750	26.7	17.8	6.82	750	11.1	23.4	750
760	26.6	17.8	6.82	760	11.1	23.3	760
770	26.4	17.7	6.82	770	11.1	23.1	770
780	26.3	17.6	6.82	780	11.1	23.0	780
790	2.61	17.5	6.80	790	11.0	22.9	790
800	26.0	17.4	6.80	800	11.0	22.8	800

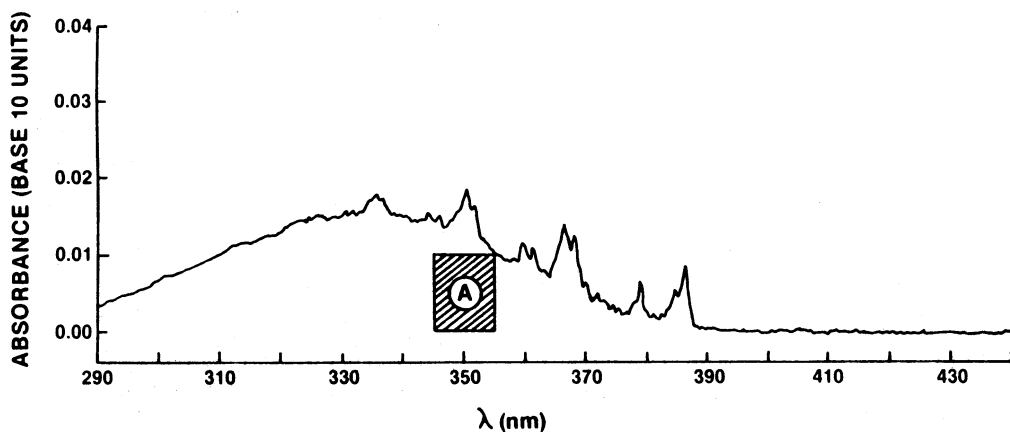
^a J_{λ} values are in units of 10^{19} photons cm^{-2} day⁻¹.

^b Wavelength intervals are uniformly 10 nm wide, extending from 5 nm lower than the center wavelength to 5 nm higher. Thus, the first interval centered on 290 extends from 285–295 nm

(4) **Example of application of methodology.** (i) Consider a chemical plant located in Freeport, Texas, which produces acrolein ($\text{CH}_2=\text{CHCHO}$) continuously every day of the year. Despite the fact that all acrolein wastes, including vented vapors, are treated in a waste-treatment plant, some acrolein escapes into the atmosphere. The chemical plant is located at 29° north latitude. Estimate the maximum sunlight direct photolysis rate constant and the corresponding minimum half-life in the atmosphere in the vicinity of the plant for the winter and summer season solstices under clear sky conditions.

(ii) The vapor phase spectrum of acrolein was obtained by the procedure outlined in this test method and is depicted in the following Figure 3:

FIGURE 3—GAS PHASE ABSORPTION SPECTRUM OF ACROLEIN



The spectral data were taken from the work of Pitts et al. (1981) under paragraph (d)(2) of this guideline. The pathlength of the sample gas absorption cell was measured according to the recommended procedure and was found to be 9.98 cm. The gas absorption cell contained 6.52×10^{16} molecules cm^{-1} of acrolein. A compensating polar planimeter was used to integrate each 10 nm interval throughout the region of absorption from 285 nm to 425 nm in both the sample and blank spectra. Based on triplicate measurements, one square, corresponding to 0.001 absorbance units (A), was found to be 0.148 vernier units (v.u.). The mean absorbance (A_λ) was obtained from these spectra and the mean cross section (σ'_λ) was obtained using Equation 7 under paragraph (d)(1)(i)(A) of this guideline for each wavelength interval, centered at λ . All the results are summarized in the following Table 5:

Table 5—Absorbance and Cross Section for Acrolein Vapor¹

Wavelength λ (nm)	Wavelength interval (nm)	Mean absorbance (A_λ)	Mean cross section σ'_λ ($\text{cm}^2 \text{ molecule}^{-1}$)
290	285–295	0.0037	5.69×10^{-21}
300	295–305	0.0066	1.01×10^{-20}
310	305–315	0.0104	1.60×10^{-20}
320	315–325	0.0137	2.11×10^{-20}
330	325–335	0.0156	2.40×10^{-20}
340	335–345	0.0156	2.40×10^{-20}
350	345–355	0.0151	2.32×10^{-20}
360	355–365	0.0096	1.48×10^{-20}
370	365–375	0.0073	1.12×10^{-20}
380	375–385	0.0031	4.76×10^{-21}
390	385–395	0.0016	2.46×10^{-21}
400	395–405	0.0004	6.15×10^{-22}
410	405–415	0.0003	4.61×10^{-22}
420	415–425	0.0000	0.00

¹ 6.52×10^{16} molecules cm^{-3} in a 9.98 cm gas absorption cell

(iii) A sample calculation is given for the wavelength $\lambda = 305$ nm, centered over the wavelength interval 345 to 355 nm. For convenience, the area A, corresponding to 100 squares was blocked off in this absorption area and was not integrated with the planimeter. The average vernier reading of the remaining absorption area was 7.2 v.u. Hence,

$$7.2 \text{ v.u.}/(0.148 \text{ v.u./square}) = 49 \text{ squares}$$

and the total area in the spectrum in the wavelength interval 345 to 355, centered at $\lambda = 350$ nm, is 149 squares. This number of squares corresponds to 0.0149 absorbance units:

$$(149 \text{ squares})(0.001 \text{ A/square})/10 = 0.0149 \text{ A}$$

From the blank spectrum, the baseline absorbance ($A_{\lambda \text{ blank}}$) over this interval was -0.0001 . The sample trace lay at $+0.0001$ absorbance units relative to a zero point at 450 nm. The observed sample absorbance is then equal to 0.0150 ($0.0149 + 0.0001$). The absolute corrected absorbance for the sample is given by

$$A^{\text{corr}}_{\lambda \text{ sample}} = A^{\text{obs}}_{\lambda \text{ sample}} - A_{\lambda \text{ blank}}$$

$$A^{\text{corr}}_{\lambda \text{ sample}} = 0.0150 - (-0.0001) = 0.0151 \text{ A}$$

(iv) Using Equation 7 under paragraph (d)(1)(i)(A) of this guideline and the values for the corrected sample absorbance, l , and C , the mean cross section for the wavelength $\lambda = 350$ nm, centered over the wavelength interval 345–355 nm, is

$$\begin{aligned} \sigma'_\lambda &= 0.0151/(6.52 \times 10^{16} \text{ molecules cm}^{-3})(9.98 \text{ cm}) \\ &= 2.3 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1} \end{aligned}$$

(v) Since the plant is located at 29° north latitude, the closest J_λ values are at 30° north latitude. These values are obtained from Table 2 under

paragraph (d)(3) of this guideline and are summarized in Table 6 for the summer and winter season solstices. Using the data in Tables 5 and 6 under paragraph (d)(4)(ii) of this guideline, the products $\sigma_{\lambda}J_{\lambda}$ are calculated for each wavelength interval, centered at λ , and the results are summarized in the following Table 6 for each of the solstices:

Summer	Winter
$(k_{pE})_{\max} = 16.9 \text{ days}^{-1}$	$(k_{pE})_{\max} = 7.60 \text{ days}^{-1}$
$(t_{1/2})_{\min} = 0.041 \text{ days}$	$(t_{1/2})_{\max} = 0.091 \text{ days}$

The terms $\Sigma\sigma_{\lambda}J_{\lambda}$ are also summarized for each solstice at the bottom of Table 6. Using these data in Equations 3 and 4 yields:

Summer	Winter
$(k_{pE})_{\max} = 16.9 \text{ days}^{-1}$	$(k_{pE})_{\max} = 7.60 \text{ days}^{-1}$
$(t_{1/2})_{\min} = 0.041 \text{ days}$	$(t_{1/2})_{\min} = 0.091 \text{ days}$

Thus, acrolein transforms rapidly under clear sky conditions in the vicinity of the plant at Freeport, Texas on the summer and winter season solstices

Table 6—Calculation of $(k_{pE})_{\max}$ For Acrolein Vapor; Rate at 30 °N On Winter and Summer Solstices

Wavelength λ (nm)	Wavelength interval (nm)	Summer solstice		Winter solstice	
		J_{λ} photons (cm ⁻² day ⁻¹)	$\sigma'_{\lambda}J_{\lambda}$ (day ⁻¹)	J_{λ} photons (cm ⁻² day ⁻¹)	$\sigma'_{\lambda}J_{\lambda}$ (day ⁻¹)
290	285–295	1.0×10^{15}	0.000	2.1×10^{12}	0.000
300	295–305	8.31×10^{17}	0.008	8.35×10^{16}	0.001
310	305–315	1.14×10^{19}	0.182	3.00×10^{18}	0.048
320	315–325	2.84×10^{19}	0.599	1.06×10^{19}	0.224
330	325–335	5.02×10^{19}	1.205	2.13×10^{19}	0.511
340	335–345	5.49×10^{19}	1.318	2.48×10^{19}	0.595
350	345–355	6.28×10^{19}	1.457	2.89×10^{19}	0.671
360	355–365	6.49×10^{19}	0.961	3.10×10^{19}	0.459
370	365–375	8.09×10^{19}	0.906	3.95×10^{19}	0.442
380	375–385	7.93×10^{19}	0.378	3.95×10^{19}	0.188
390	385–395	8.12×10^{19}	0.200	4.12×10^{19}	0.101
400	395–405	1.11×10^{20}	0.068	5.73×10^{19}	0.035
410	405–415	1.41×10^{20}	0.065	7.37×10^{19}	0.034
420	415–425	1.47×10^{20}	0.000	7.81×10^{19}	0.000
.....			$\Sigma\sigma'_{\lambda}J_{\lambda} = 7.34_7$		$\Sigma\sigma'_{\lambda}J_{\lambda} = 3.30_4$

(5) Operation of the gas handling system. The following procedure briefly describes the recommended typical and detailed operation of a gas handling system

(i) Close all stopcocks and turn on the rotary pump (A). Open stopcock 4 and place a Dewar containing liquid nitrogen around trap (D). Measure the pressure with the thermocouple gauge H_1 . When the pressure is less than 0.1 torr (0.013 kPa) open stopcocks 5 and 10, pump out this portion of the manifold, and measure the pressure with the thermocouple gauge H_2 . When the pressure falls below 10^{-2} torr (1.3×10^{-3} kPa), open stopcock 7 and evacuate F containing activated Linde Molecular Sieve 4A or an equivalent grade. Heat F to approximately 150 °C for 1 to 2

hours under vacuum until the pressure falls to less than 10^{-2} torr (1.3×10^{-3} kPa) as measured on thermocouple gauge H₂. Open stopcocks 6, 9, and 11 and pump until H₂ falls below 10^{-2} torr (1.3×10^{-3} kPa).

(ii) Turn on the diffusion pump (C) and when this pump has reached operating temperature, open stopcocks 2 and 3 and close stopcock 4. Pump on the manifold until the pressure is $\leq 10^{-5}$ torr (1.3×10^{-6} kPa) as measured by the ionization gauge (I) and zero on the capacitance manometer (G). It should be noted that the ionization gauge (I) should only be used when H₂ indicates a pressure less than 10^{-2} torr (1.3×10^{-3} kPa).

(iii) It is good practice, after the gas phase spectrum has been obtained, to evacuate the gas absorption cell (K) and the trap (F) prior to shutting down the gas handling system. The gas handling system can be shut down by the following procedure: (A) closing stopcocks 5 to 11; (B) switching off the diffusion pump; (C) closing stopcocks 2 and 3 and opening 4, after the diffusion pump is cool; (D) removing the Dewar from trap (D) and allowing it to warm up; (E) then closing stopcock 4 and switching off the rotary pump; and (F) opening stopcock 1 to admit air to the rotary pump, thus preventing suck-back of the rotary pump oil. With this procedure, the vacuum manifold, the trap (D), and the diffusion pump are left under vacuum. The method of cleaning the liquid reservoir (J) is left to the discretion of the tester. However, as a final step it should be cleaned with reagent grade methanol or dichloromethane as solvent and dried. It is then ready for use. In operating a vacuum system with the diffusion pump working, do not expose the diffusion pump to pressures ≥ 0.1 torr of air (1.3×10^{-2} kPa) to avoid the degradation of the pump oil

(e) **References.** The following references should be consulted for additional background information on this test guideline:

(1) Environmental Protection Agency. Mill, T. et al., Section 5. Photolysis in Air, by J.E., Davenport, *Toxic Substances Process Generation and Protocol Development*. Work Assignment 12, Draft final report. (Athens, Georgia, and Washington, DC, 1984).

(2) Mill, T. et al., *Laboratory Protocols for Evaluating the Fate of Organic Chemicals in Air and Water*. Chapter 5. EPA 600/3-82-022 (1982).

(3) Pitts, J.N., Jr. et al., *Experimental Protocol for Determining Absorption Cross Sections of Organic Chemicals*, EPA Report No. 600/3-81-051 (1981).